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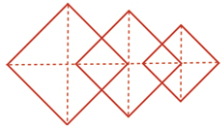
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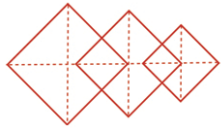




# Activation of surfaces prior to gaseous nitriding of a 3wt.% Cr carbon iron-based alloy

Speaker: Sébastien Jégou, Associate Professor  
Arts et Métiers ParisTech, MSMP Laboratory  
France

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B.Guillot, PhD, Arts et Métiers ParisTech, MSMP Laboratory



2009 – PhD – Arts et Métiers ParisTech, Aubert & Duval, France

- Gaseous Nitriding
- Residual Stresses



2010 – PostDoc – DTU, Denmark

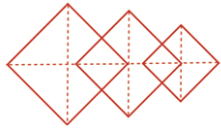
- Expanded Austenite
- Nitriding / Carburizing
- Residual Stresses



2011-... - Associate Professor – Arts et Métiers ParisTech, France

- Materials Science
- Surface Engineering



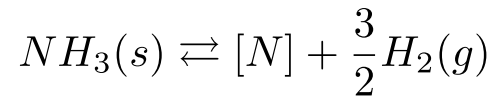


## AGENDA

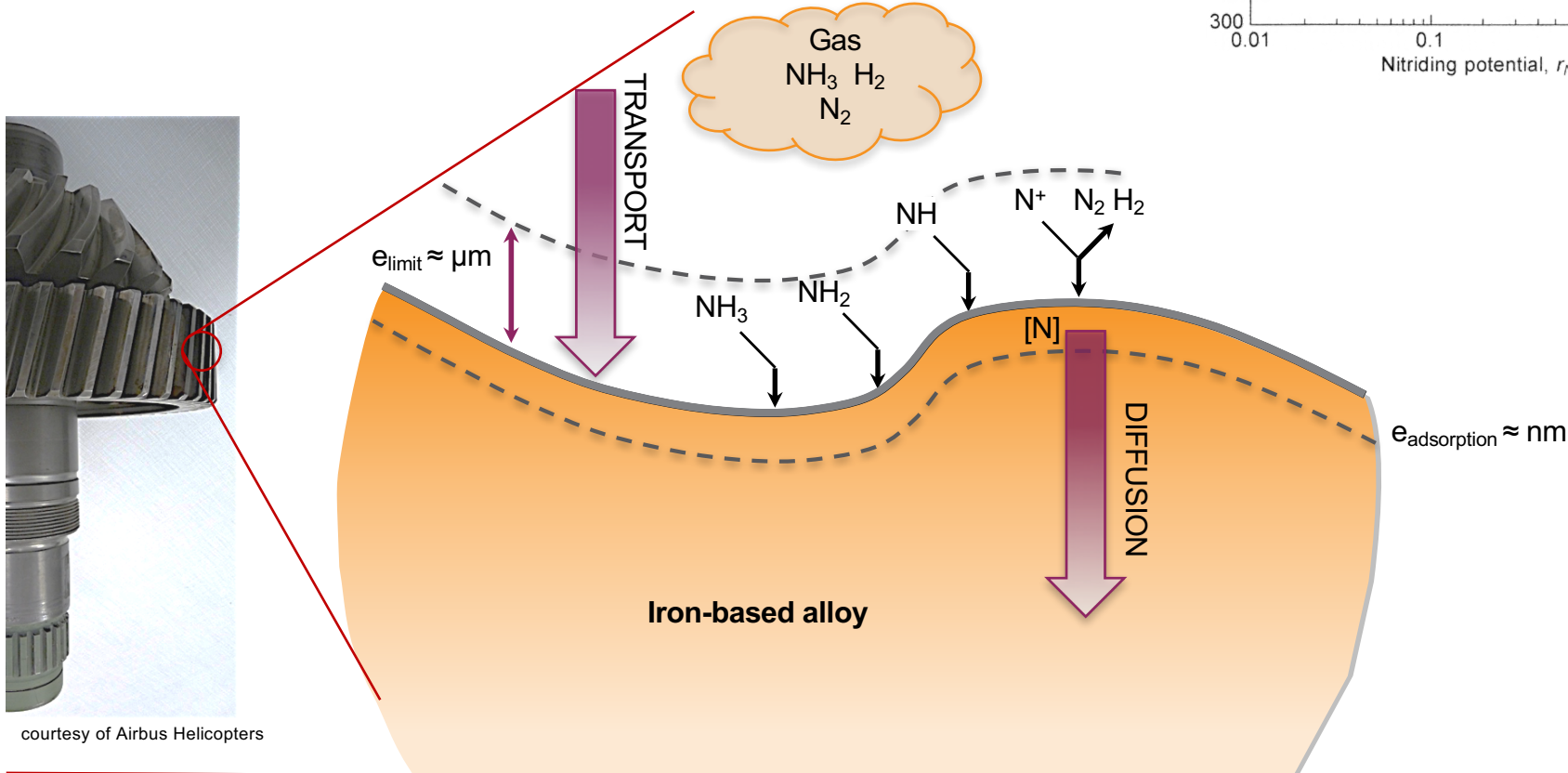
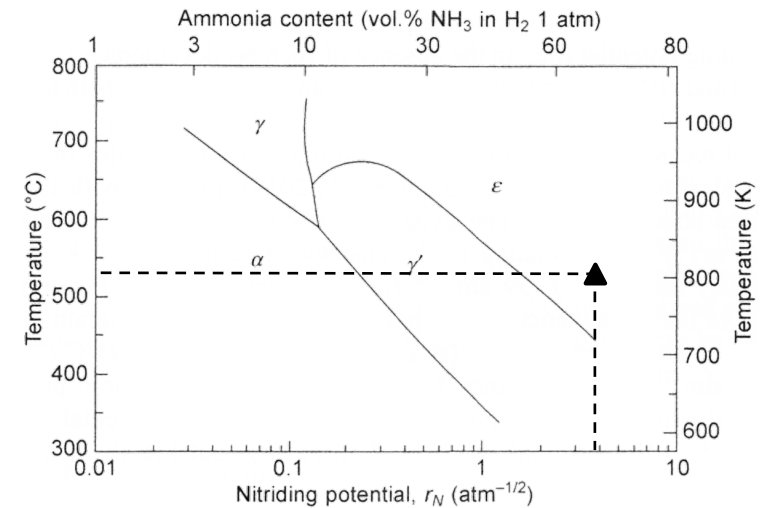
1. Introduction
2. Experiments
3. Results
4. Conclusion



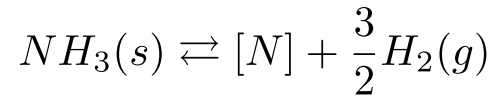
## 1. Introduction - Context



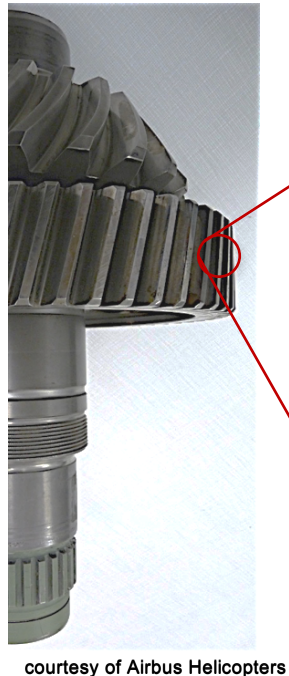
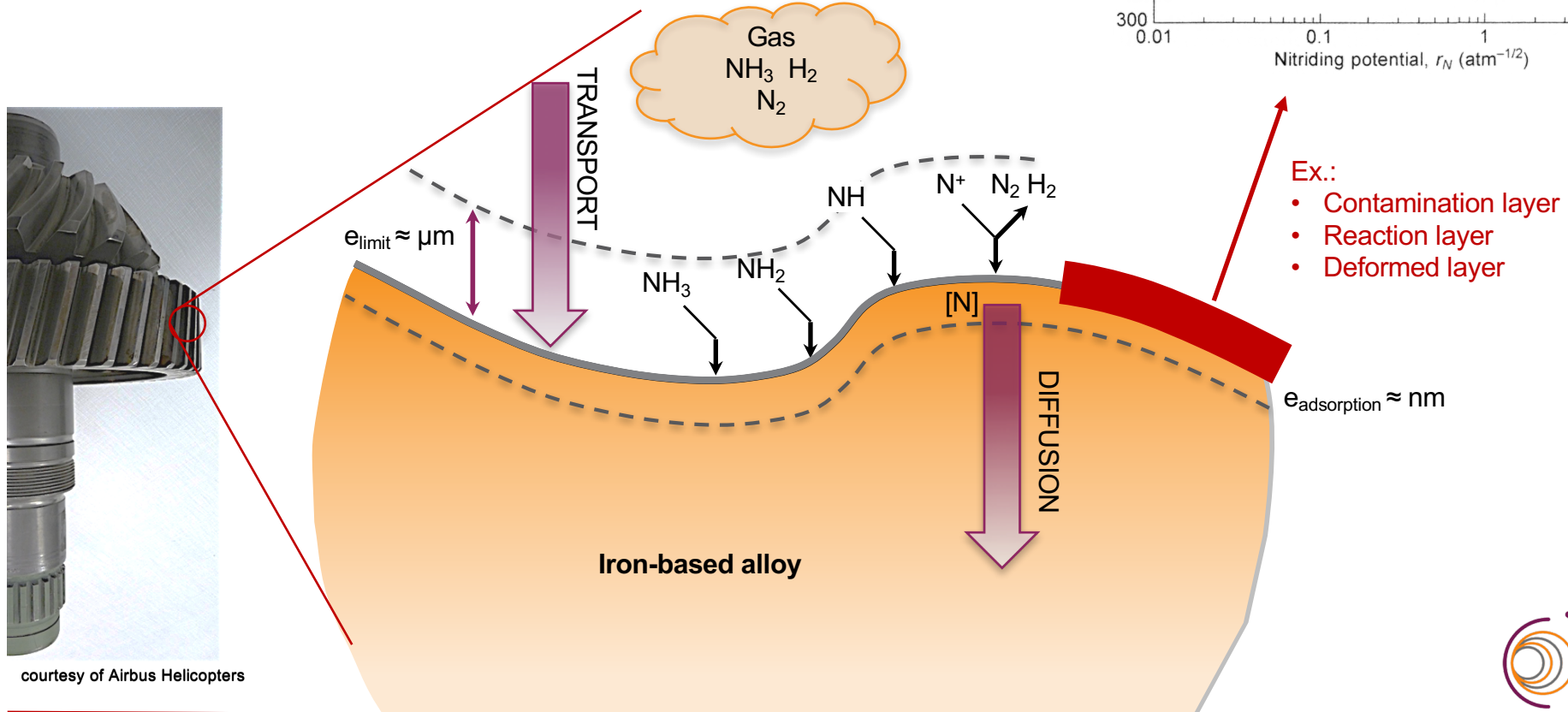
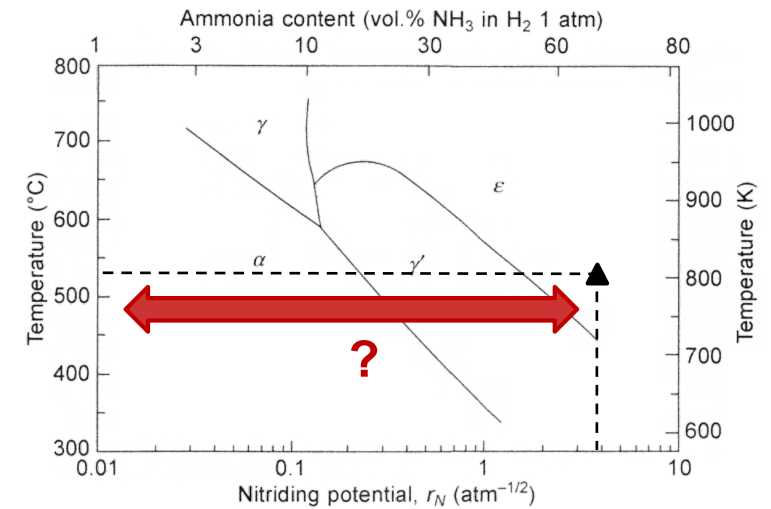
$$K_N = \frac{p_{NH_3}}{p_{H_2}^{3/2}}$$



## 1. Introduction - Context



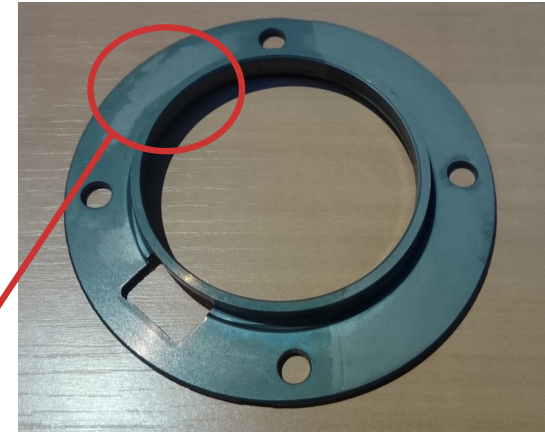
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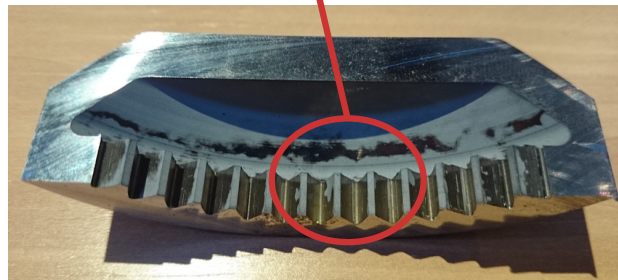


courtesy of Airbus Helicopters



courtesy of Bodycote

- Soft spot
- Lack of nitriding
- Heterogeneous nitriding

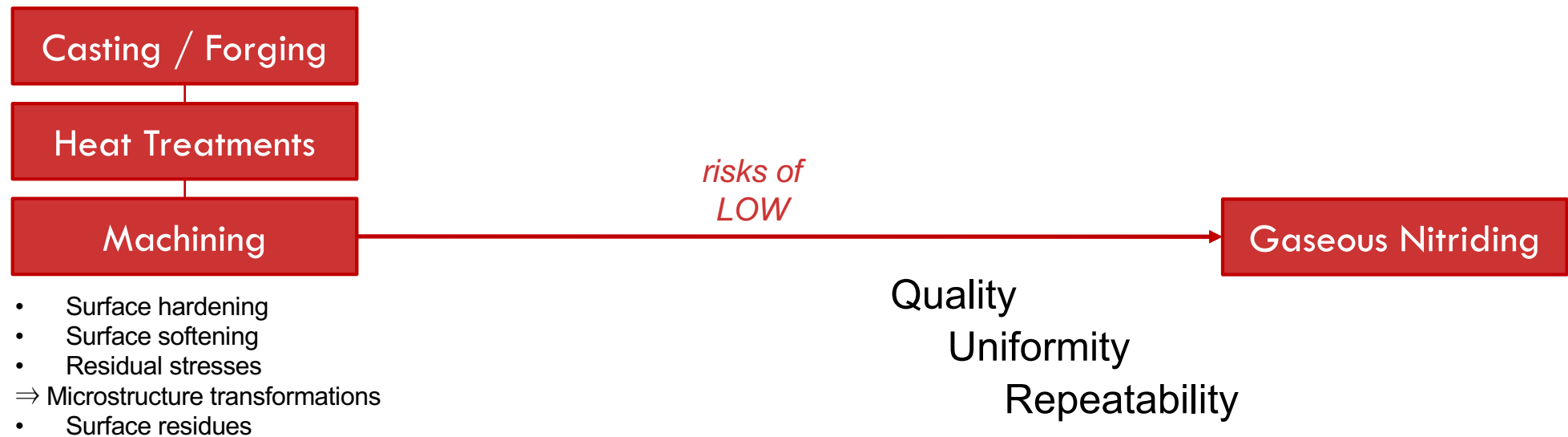


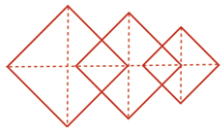
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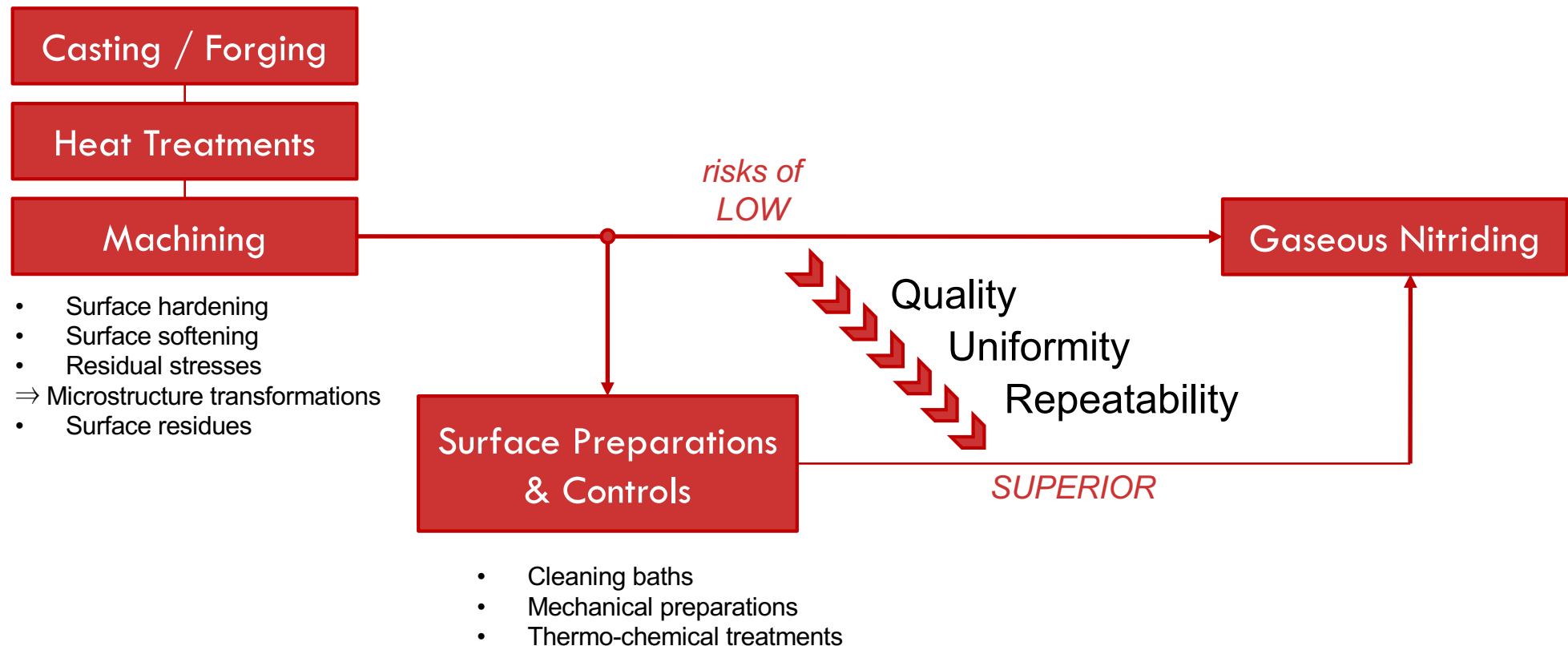


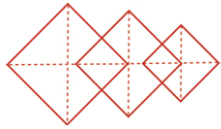
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## 1. Introduction - Context

### Surface Preparations & Controls

- Cleaning baths: residues from
  - Machining oil (sulphate, phosphate, silicon, ...)
  - Cleaning baths (anionic surfactant (sulphonates, sulphates...))

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### Surface Preparations & Controls

- Cleaning baths: residues from
  - Machining oil (sulphate, phosphate, silicon, ...)
  - Cleaning baths (anionic surfactant (sulphonates, sulphates...))
- Mechanical preparations: Sandblasting (sanding)
  - Passivation/corrosion layer
  - Heterogeneous metallurgy/microstructure



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- Cleaning baths: residues from
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- Mechanical preparations: Sandblasting (sanding)
  - Passivation/corrosion layer
  - Heterogeneous metallurgy/microstructure
- Thermo-chemical treatments: **controlled** layer (nature, thickness)
  - Oxidization
  - Phosphating (Zn, Mn)
  - ...

⇒ Surface homogeneity visual control

⇒ Protection from (heterogeneous) surface reactions

⇒ Activation of the  $\text{NH}_3$  decomposition

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### Surface Preparations & Controls

- Thermo-chemical treatments: **controlled** layer (nature, thickness)
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    - Oxidization ( $\text{NH}_3$  decomposition catalyst)
    - Phosphating (Zn, Mn)

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### Surface Preparations & Controls

- Thermo-chemical treatments: **controlled** layer (nature, thickness)
  - ⇒ Surface homogeneity **visual control**
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  - ⇒ **Activation** of the  $\text{NH}_3$  decomposition
    - Oxidization ( $\text{NH}_3$  decomposition catalyst)
    - Phosphating (Zn, Mn)
- ⇒ Better Process Flexibility: **In-situ pre-treatments**
  - cleaning
  - activation
- Oxidization : oxygen reactivity with contaminants
- Urea
 
$$\text{NH}_2 - \text{CO} - \text{NH}_2(aq, s) \rightarrow \text{HNC}(\text{O})(g) + \text{NH}_3(g) \rightarrow \text{CO}_2(g) + \text{NH}_3(g)$$
- $\text{NH}_4\text{Cl}$ 

$$\text{NH}_4\text{Cl}(aq, s) \rightarrow \text{HCl}(g) + \text{NH}_3(g)$$

⇒ Heating stage: atmosphere of Acids + N-adsorption

## 2. Experiments

- **Material: 33CrMoV12-9**
  - 17 x 13 x 5 mm<sup>3</sup>
  - Austenitized @ 920 °C, 90 min
  - Oil quenched
  - Tempered @ 640 °C, 1 h

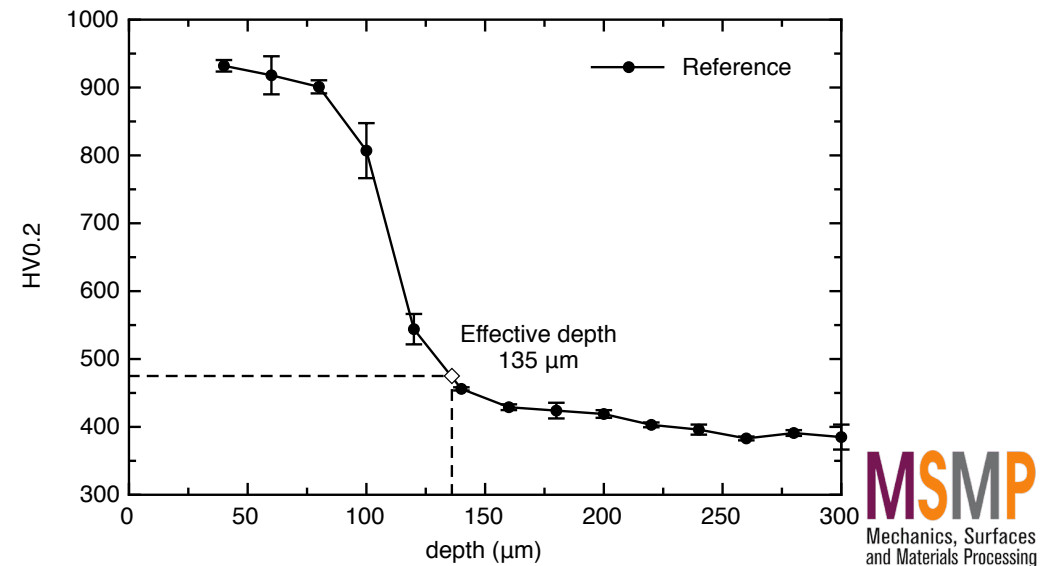
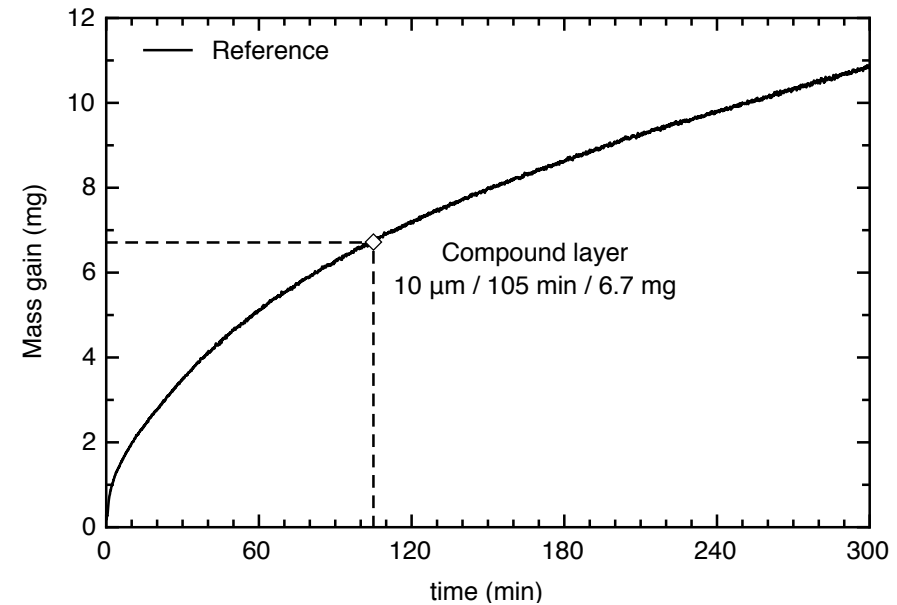
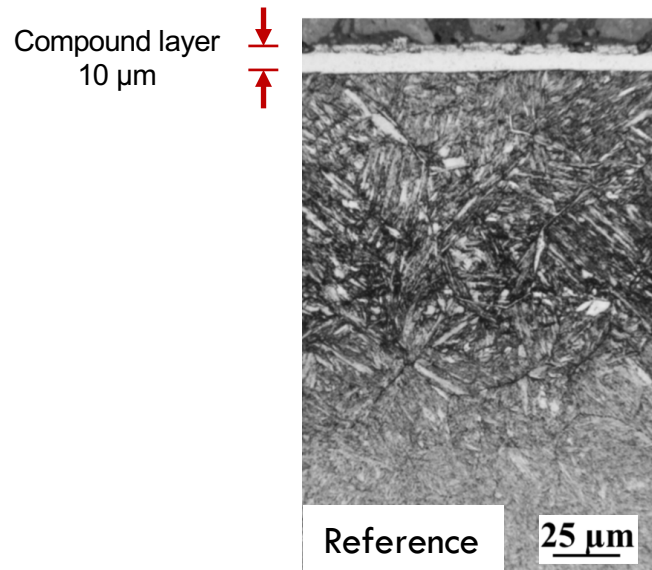
Composition (wt.%)					
C	Cr	Mo	V	Mn	Fe
0.32	2.97	0.84	0.28	0.55	bal.

- Sample preparation:
  - Degreased
  - Rinsed in water
  - Dried in alcohol

- **Surface contamination:**
  - **Water-dissolved machining oil**
    - 1 to 100 vol.%
    - 1 min dipping
    - Droplets removed
- **In-situ treatments:** 350-400 °C, 1 h
  - Vacuum Stages
  - Oxidization (O<sub>2</sub>)
  - Urea / NH<sub>4</sub>Cl
    - 200 mg
    - Neutral atmosphere
- **Gaseous Nitriding:**
  - Thermogravimetric analyser (Setsys Evo.)
  - Vacuum Stages
  - Heating/Cooling @ 10 °C.min<sup>-1</sup> under N<sub>2</sub>
  - **520 °C, 5 h, K<sub>N</sub> 3.7 atm<sup>-1/2</sup>**
  - NH<sub>3</sub>-N<sub>2</sub>-H<sub>2</sub> (200 mL.min<sup>-1</sup>)

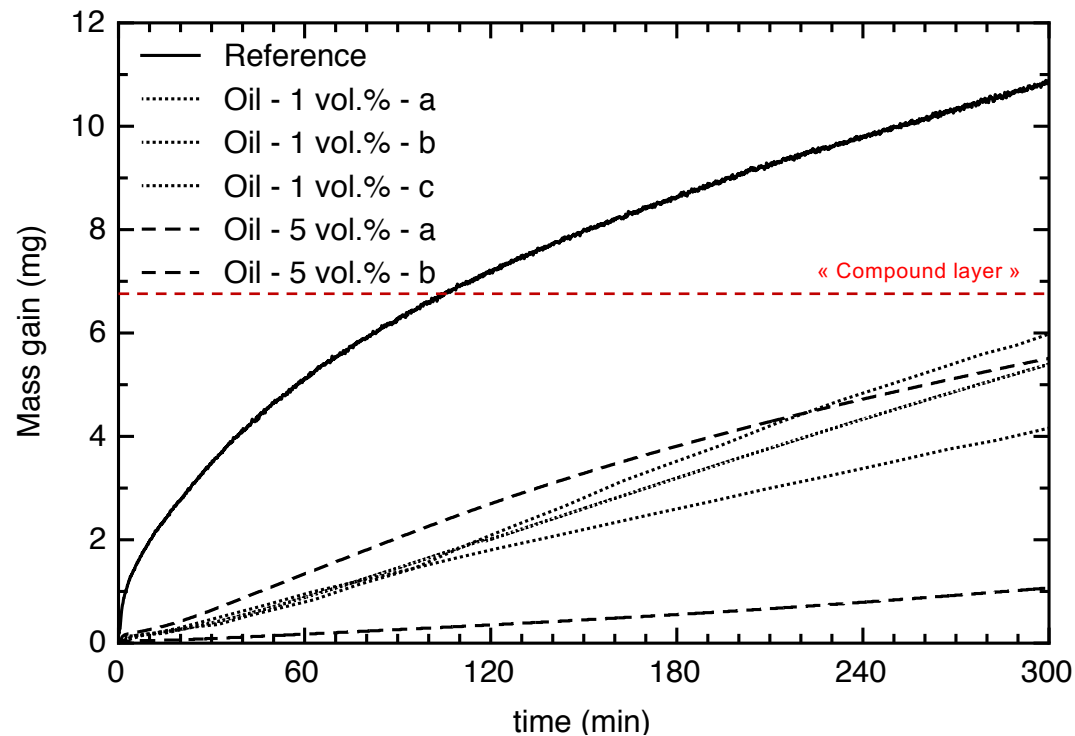
### 3. Results

#### 0. The reference



## 3. Results

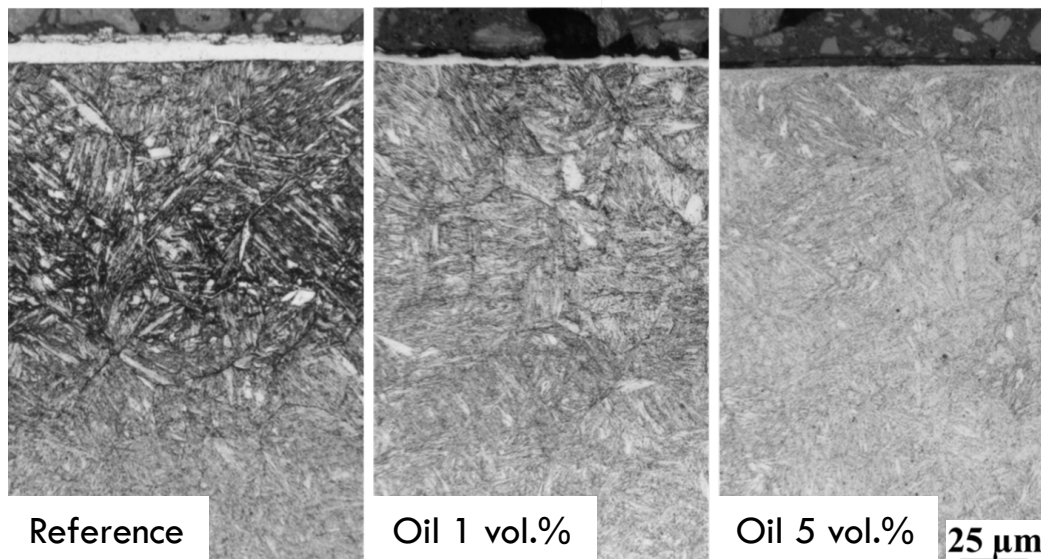
### a. Influence of water-dissolved oil contaminations



Sample	Mass gain after nitriding (mg)
Reference	10.89 ± 0.33
Oil 1 vol.% - a	5.39 (49.5 %)
Oil 1 vol.% - b	5.98 (54.9 %)
Oil 1 vol.% - c	4.16 (38.2 %)
Oil 5 vol.% - a	1.07 (9.8 %)
Oil 5 vol.% - b	5.51 (50.6 %)

## 3. Results

### a. Influence of water-dissolved oil contaminations



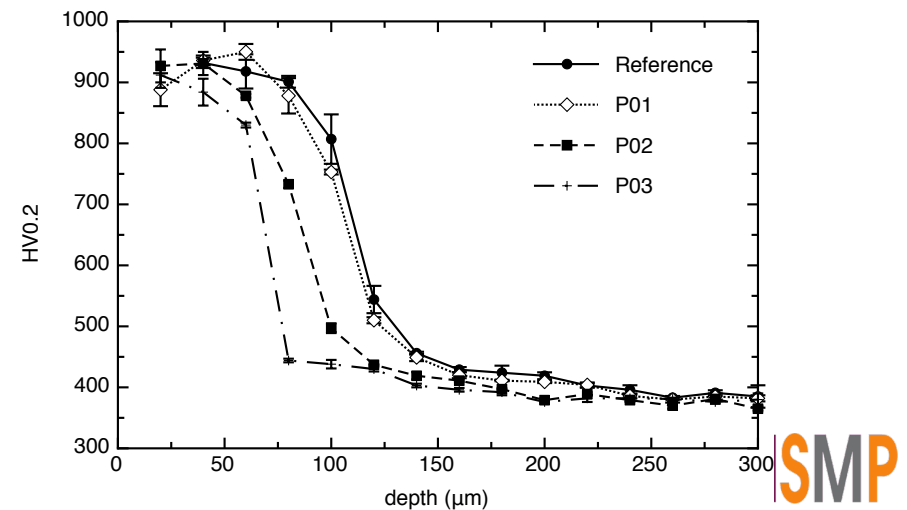
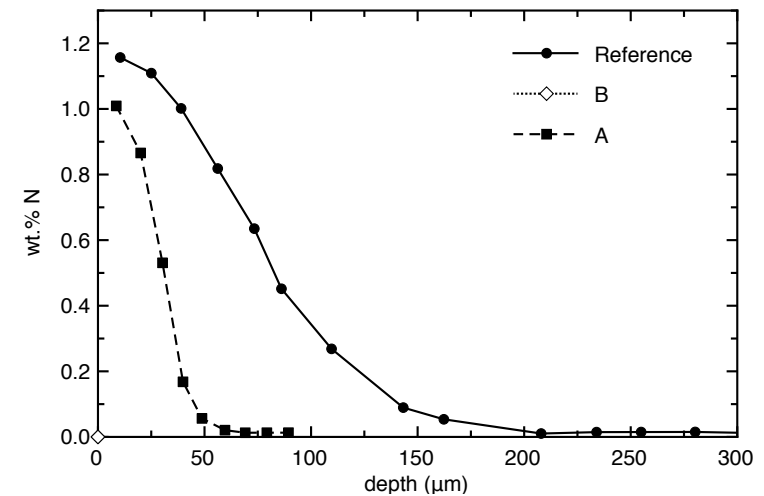
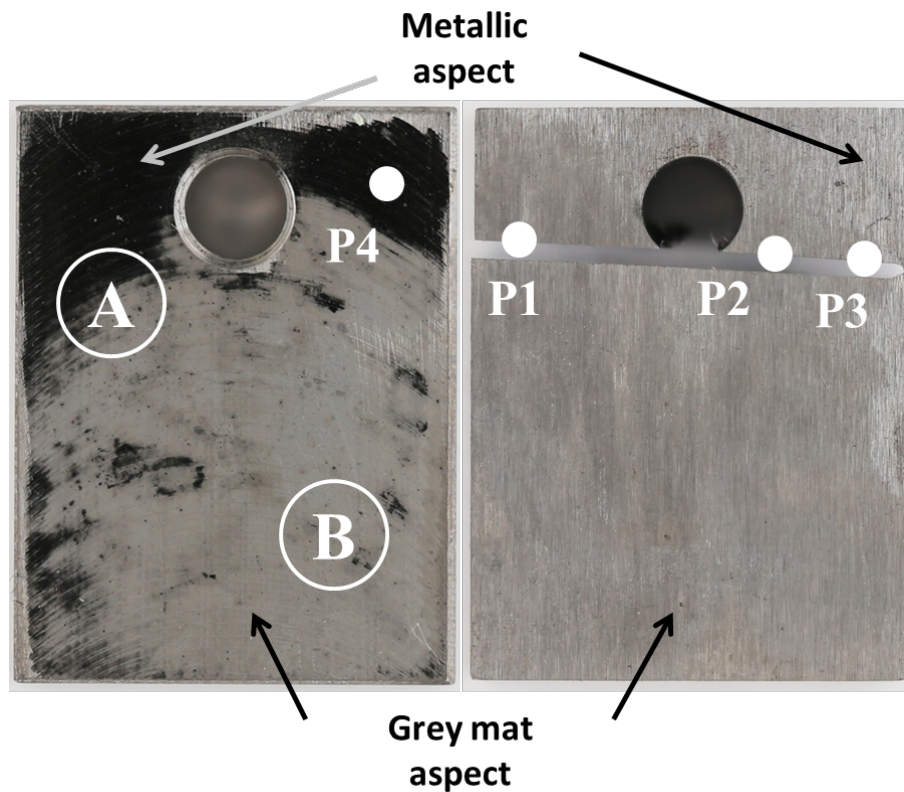
Sample	Mass gain after nitriding (mg)
Reference	10.89 $\pm$ 0.33
Oil 1 vol.% - $\alpha$	5.39 (49.5 %)
Oil 5 vol.% - $\alpha$	1.07 (9.8 %)



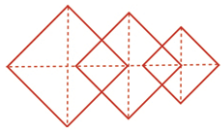
### 3. Results

#### a. Influence of water-dissolved oil contaminations

##### i. Oil 1 vol.%



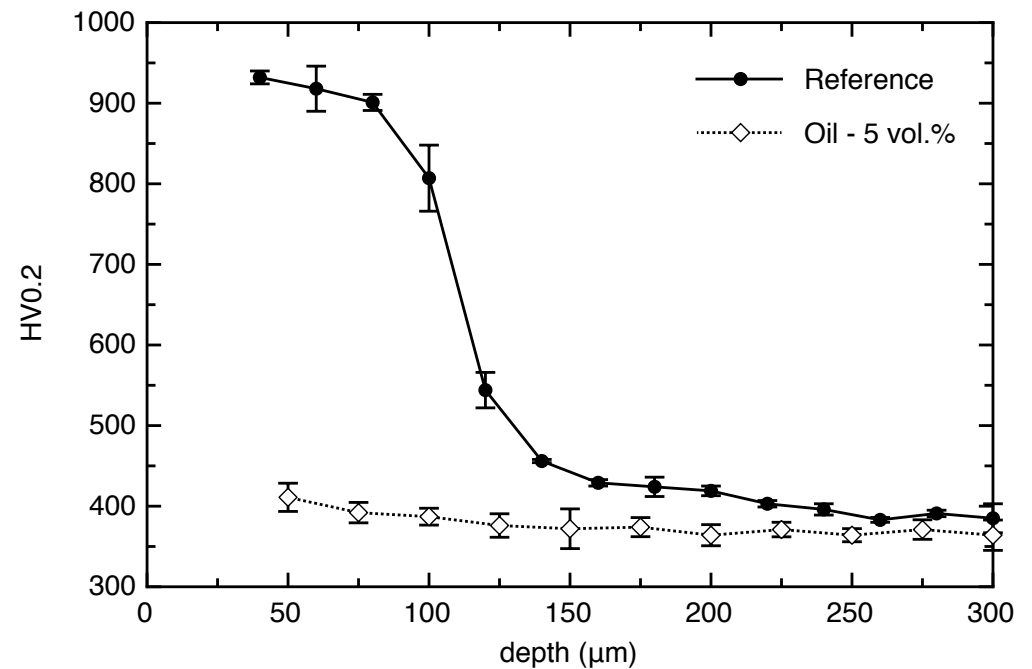
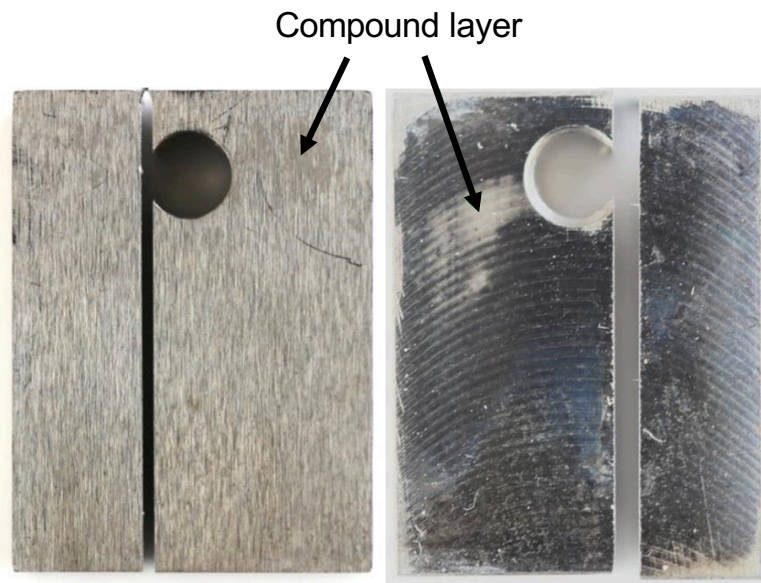


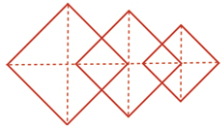


### 3. Results

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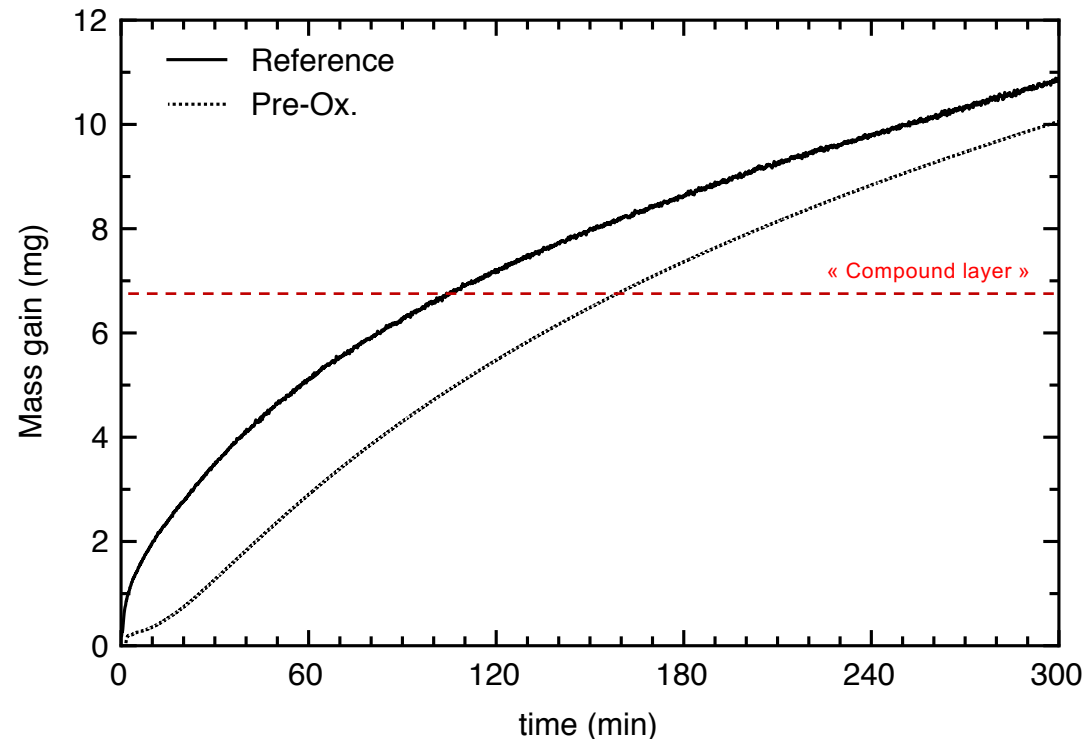
##### ii. Oil 5 vol.%

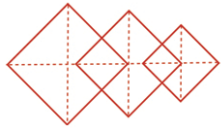




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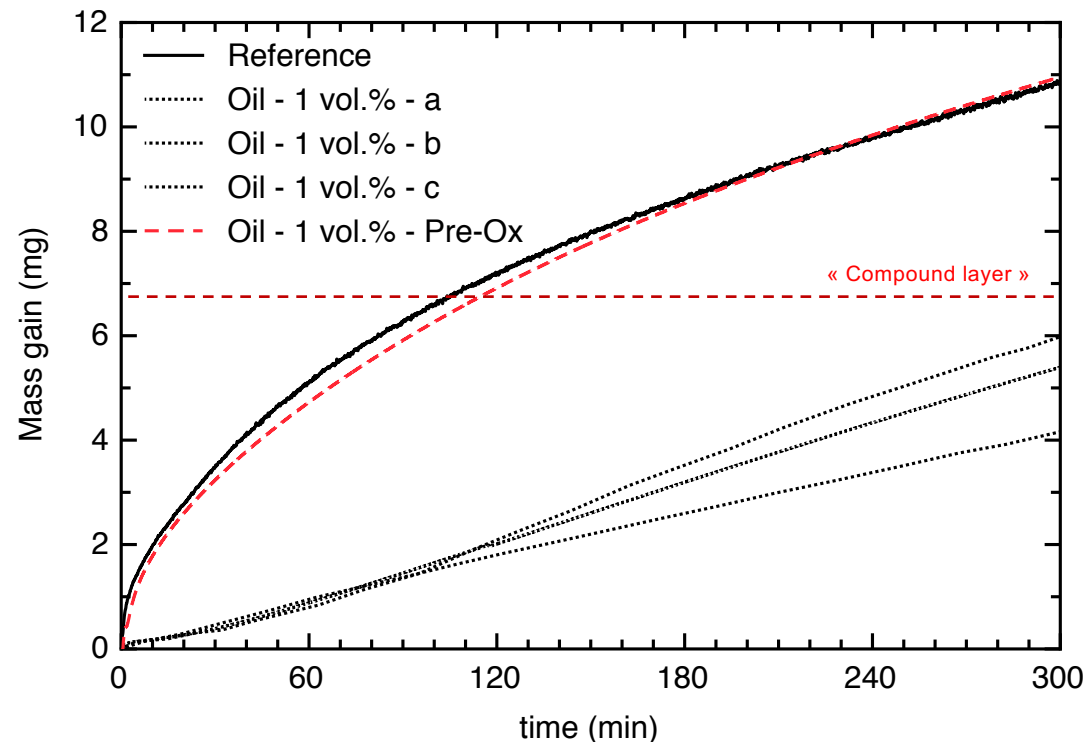
#### b. Influence of pre-oxidization ( $O_2$ , 350 °C, 1h)

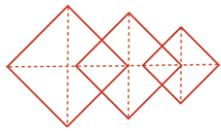




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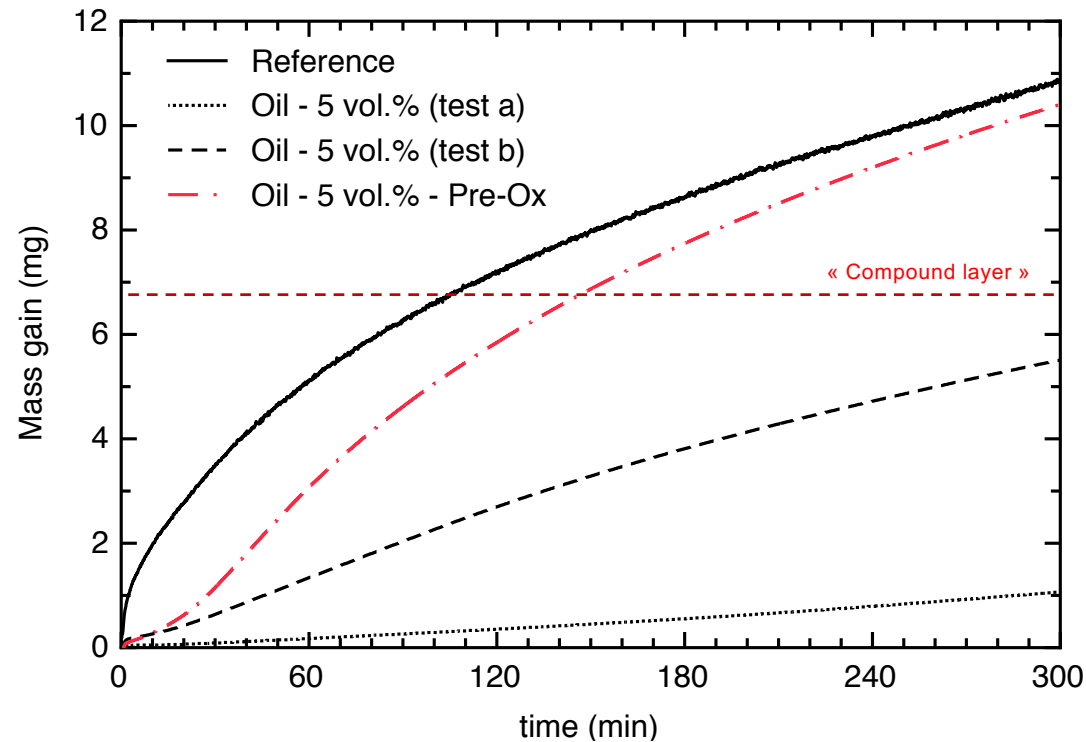
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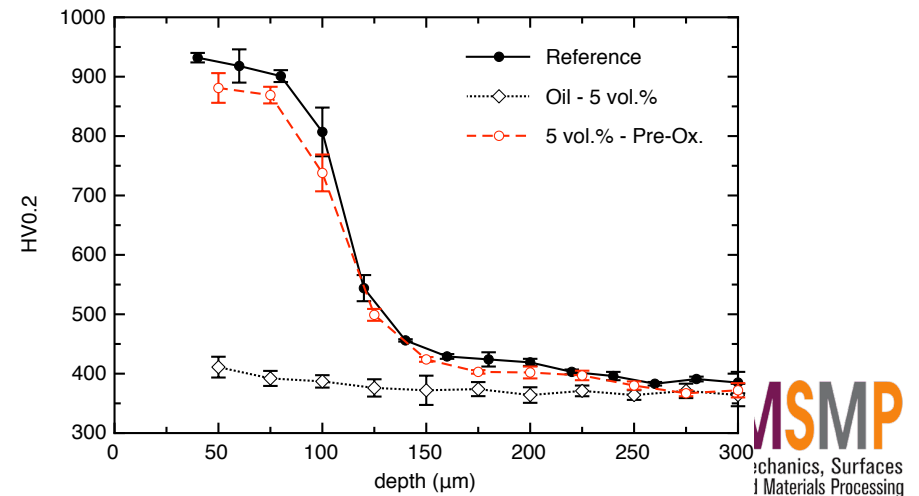
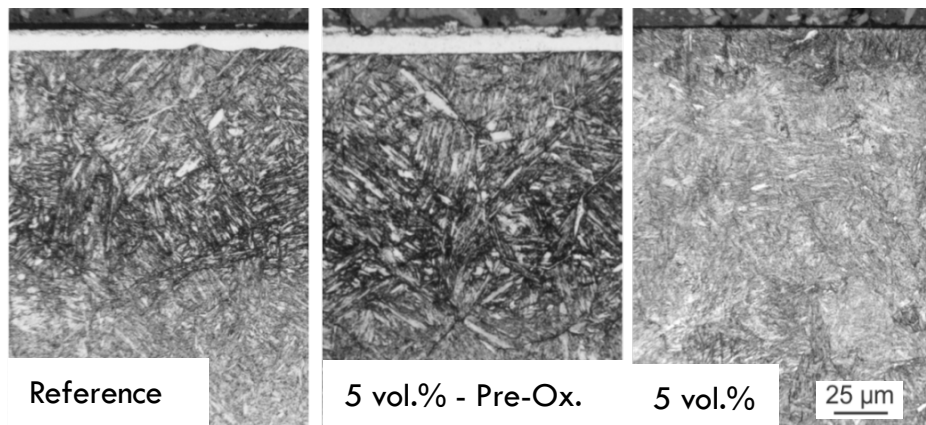
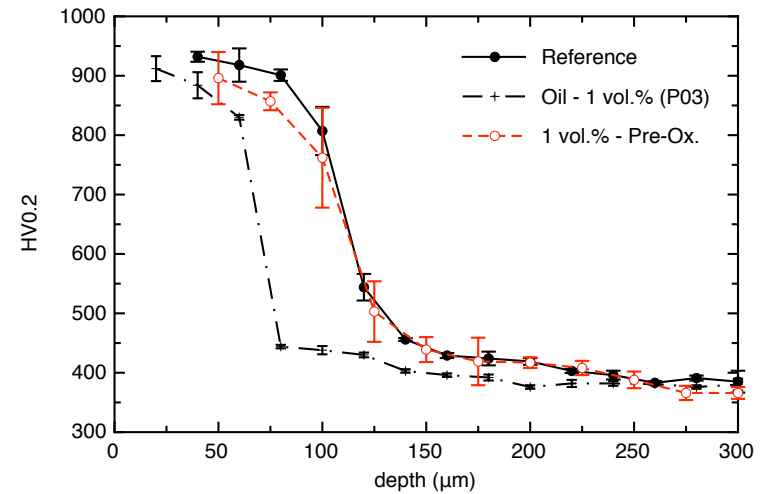
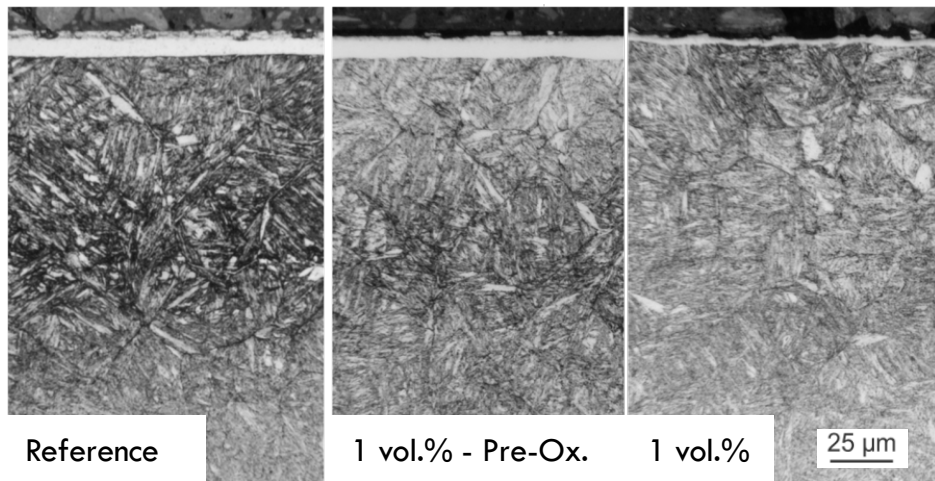
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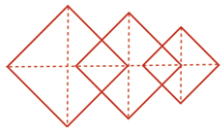
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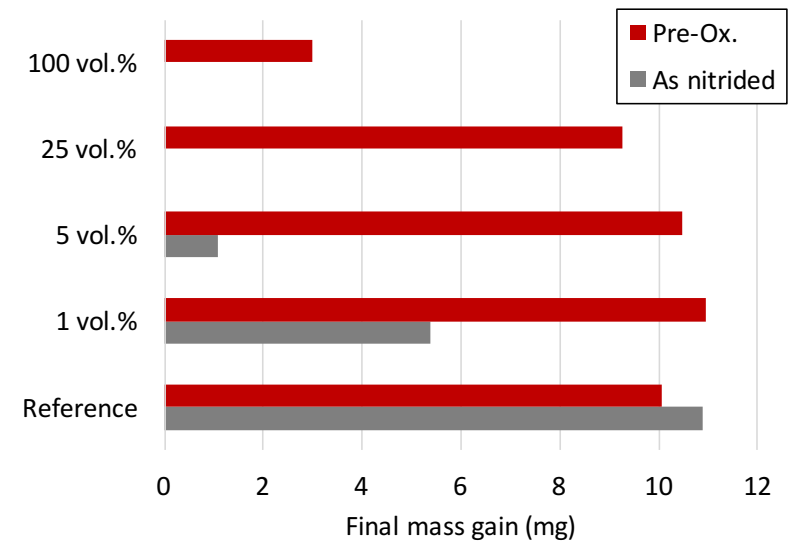
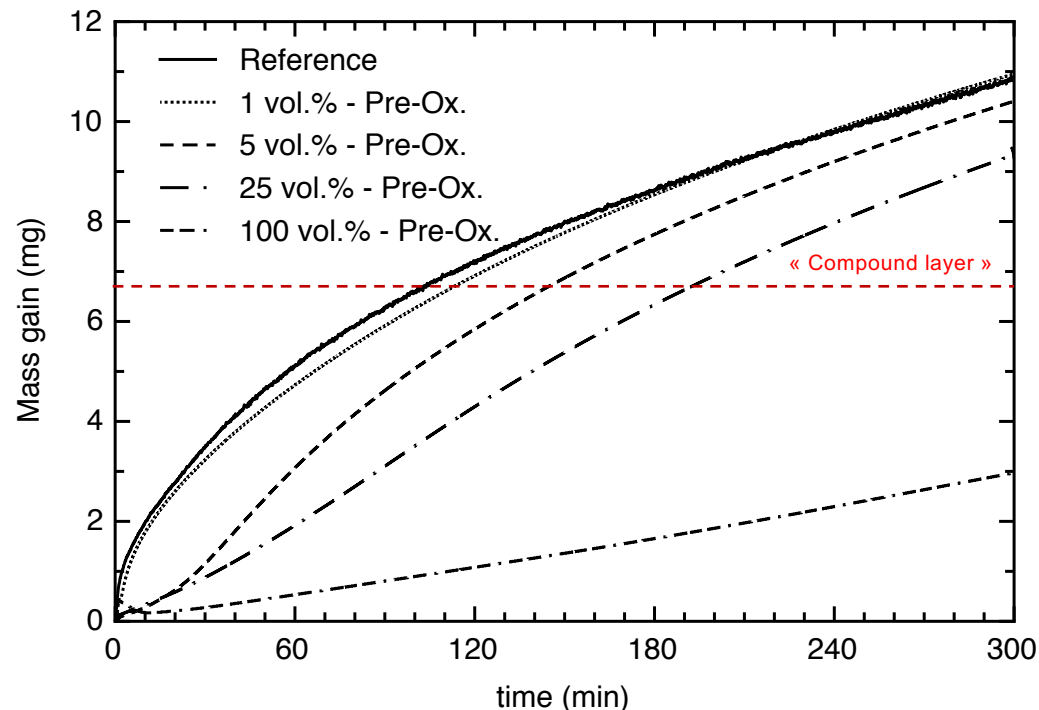
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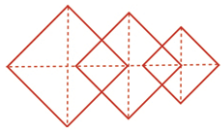




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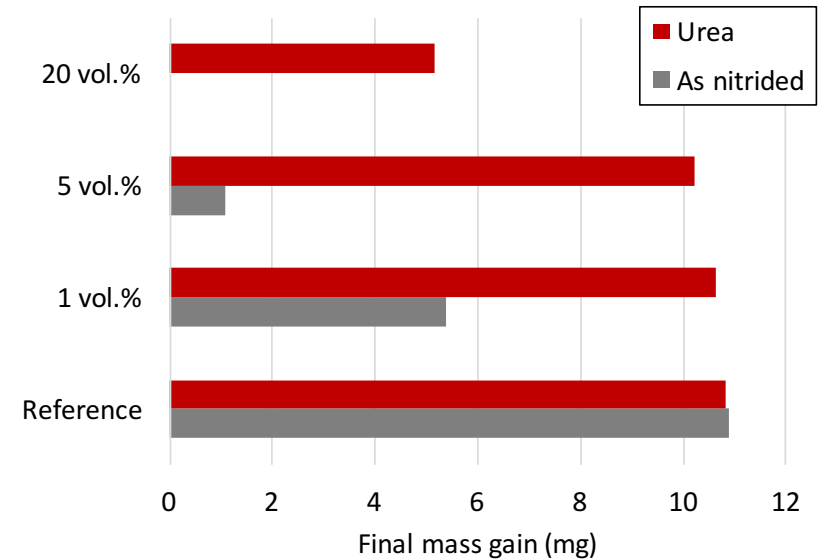
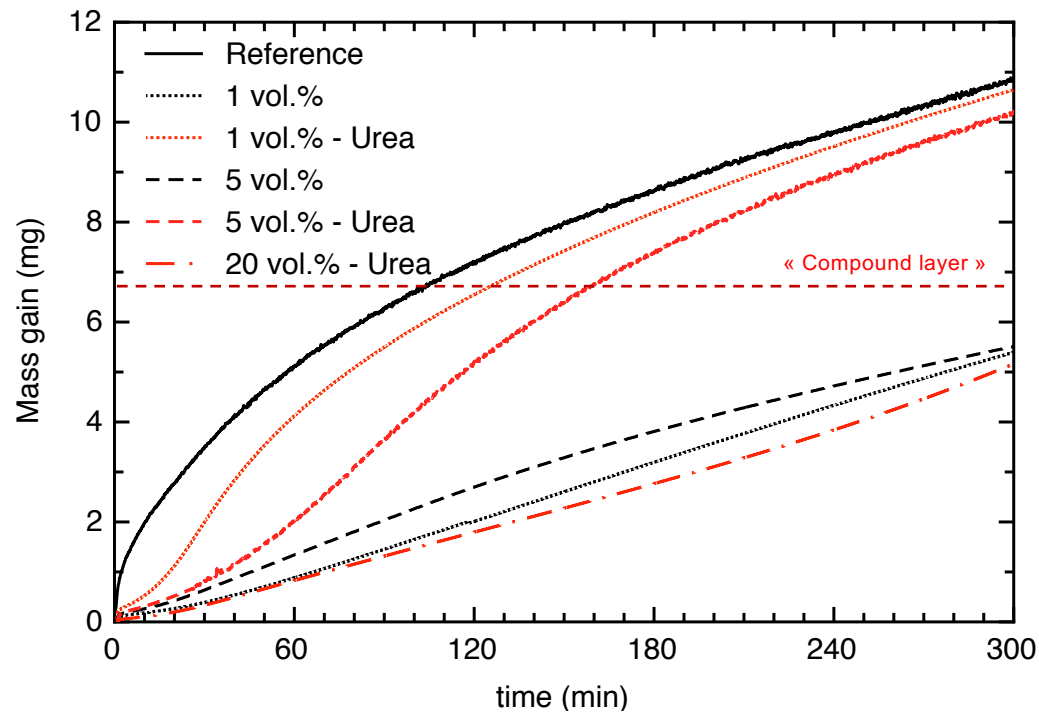
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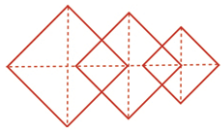


### 3. Results

#### c. Influence of urea

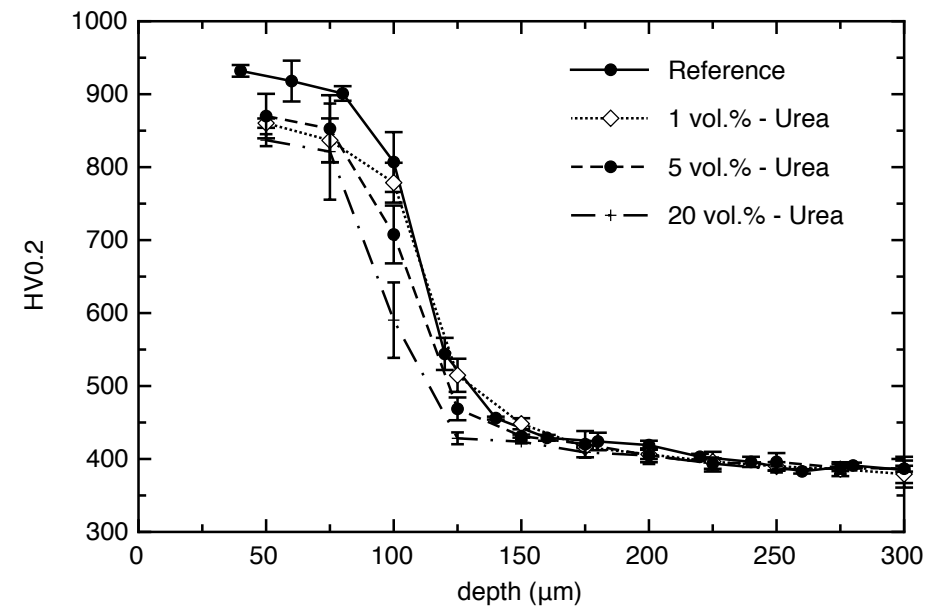
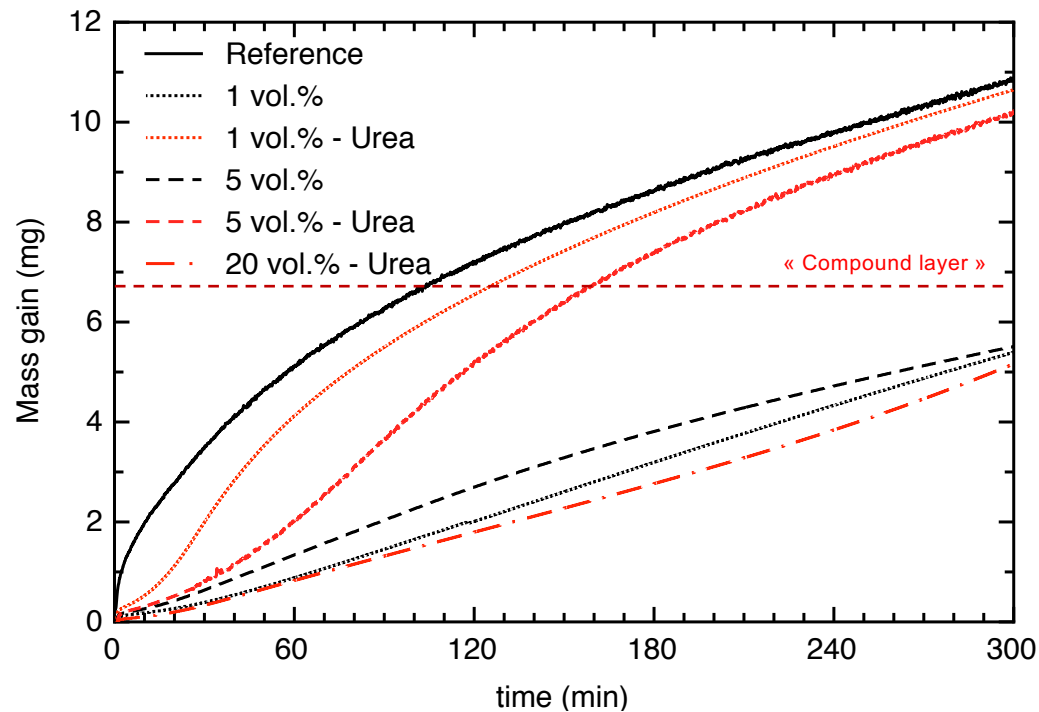




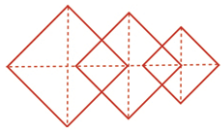


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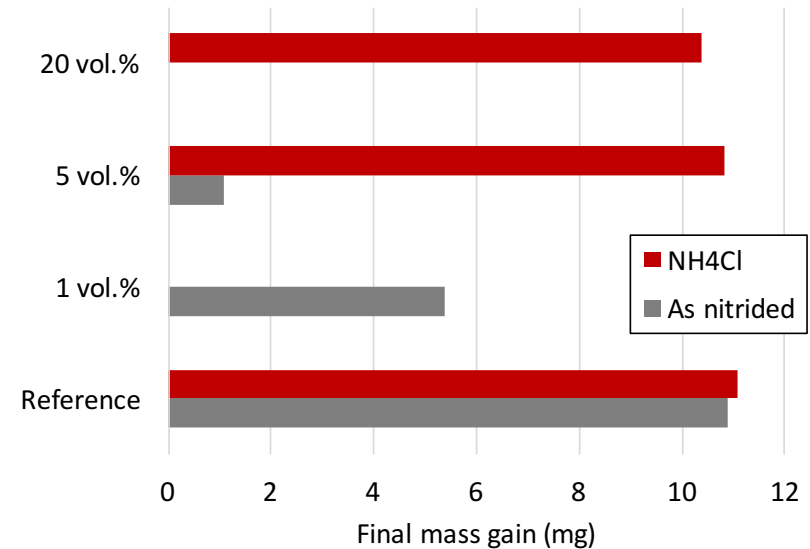
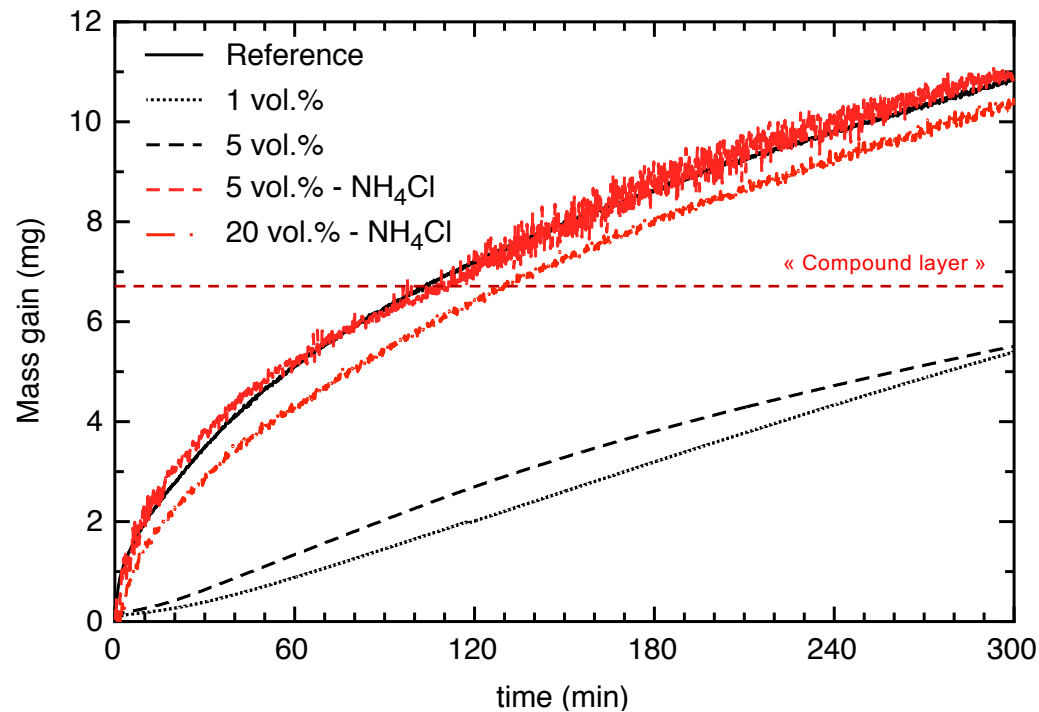






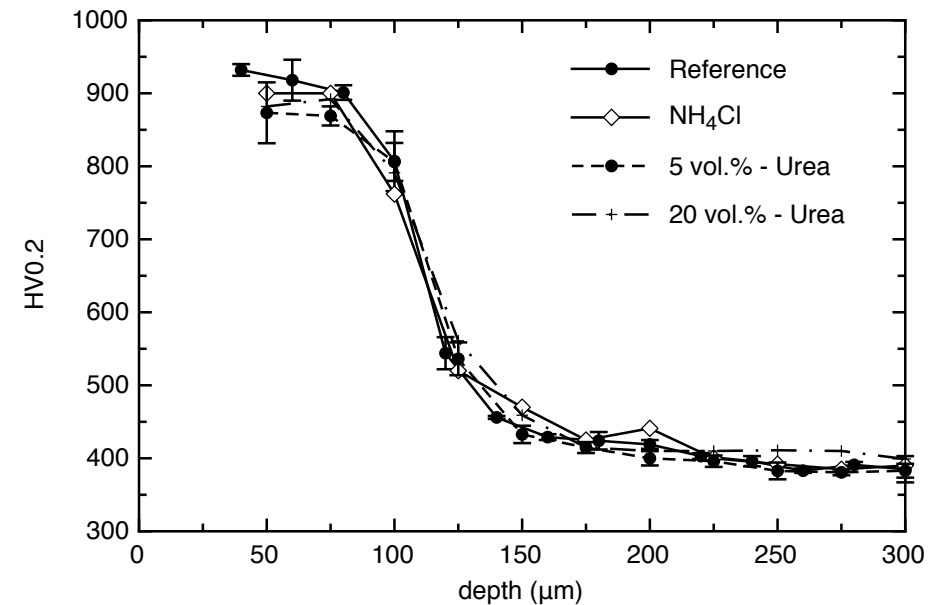
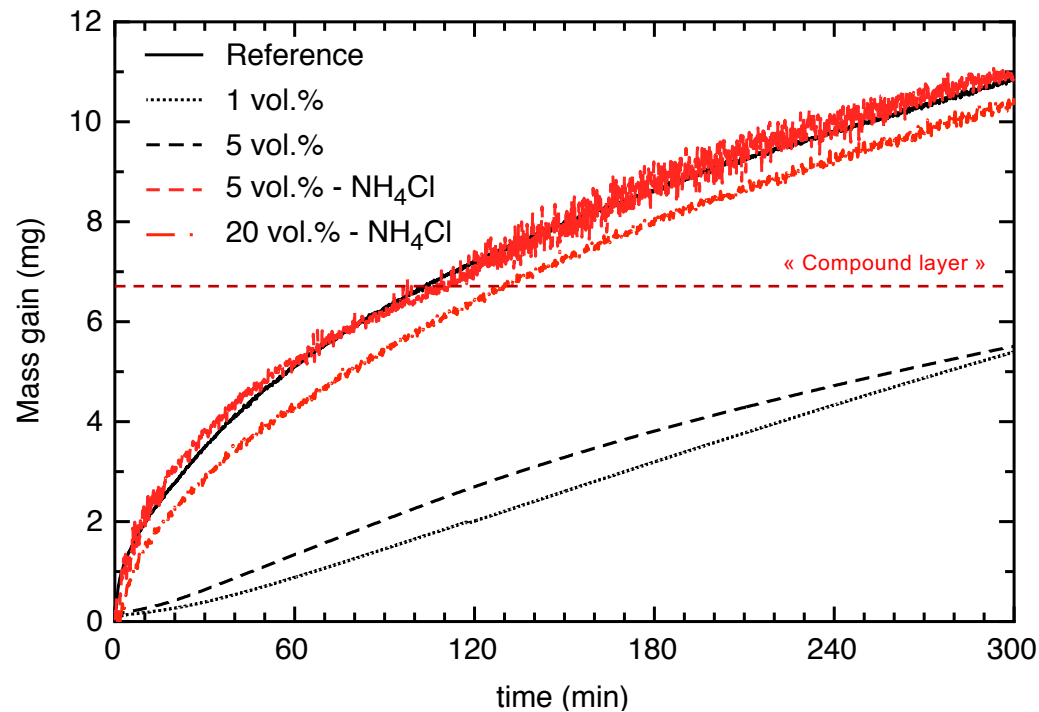
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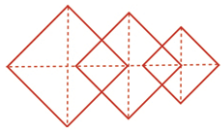
#### d. Influence of $\text{NH}_4\text{Cl}$



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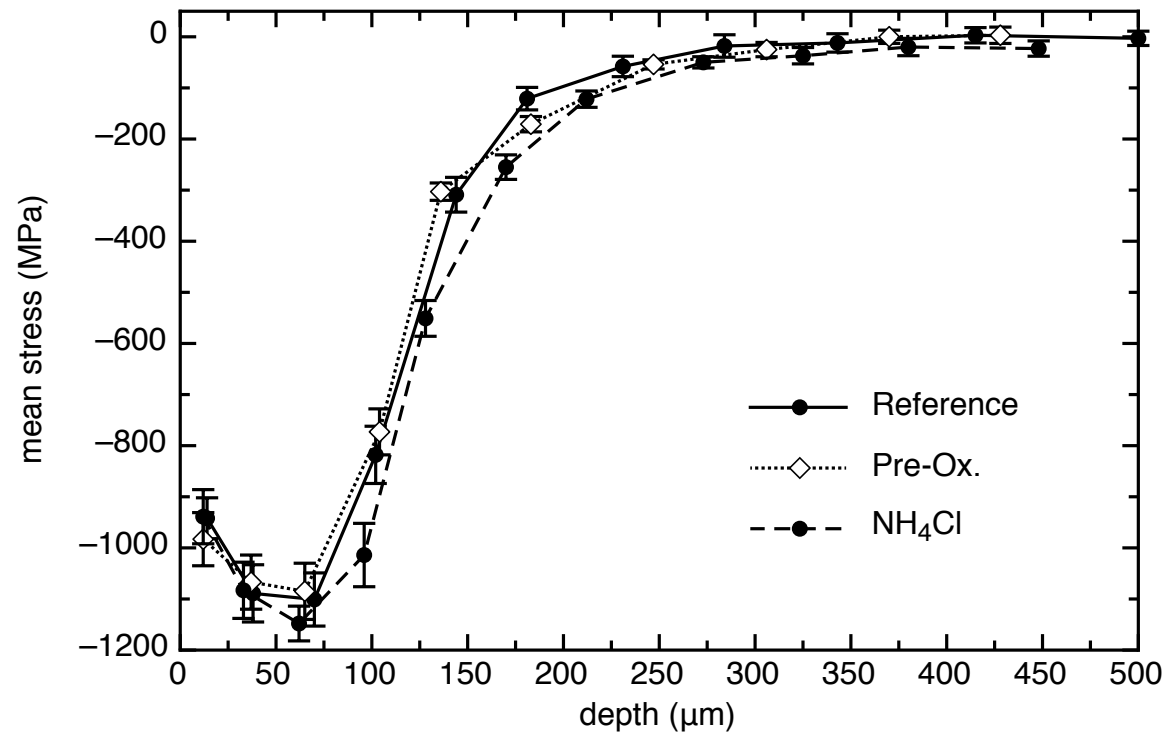
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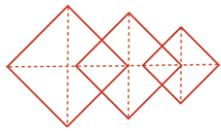




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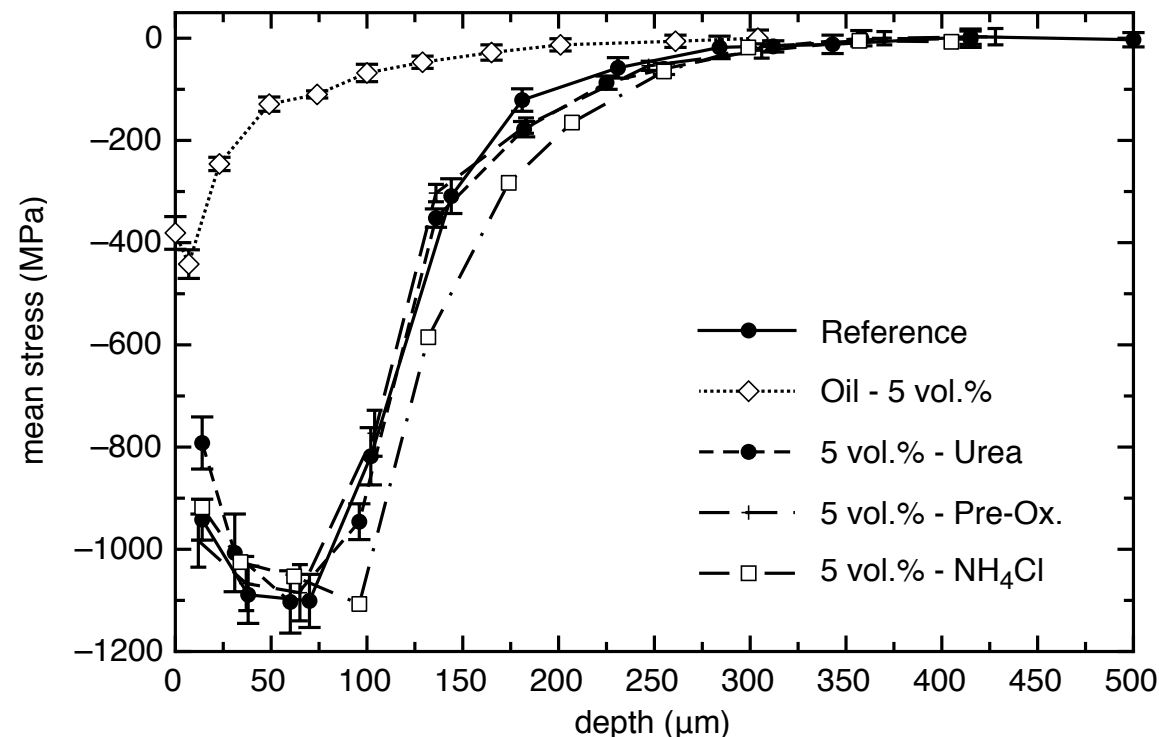
#### e. Pre-treatments & residual stresses

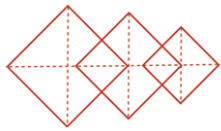




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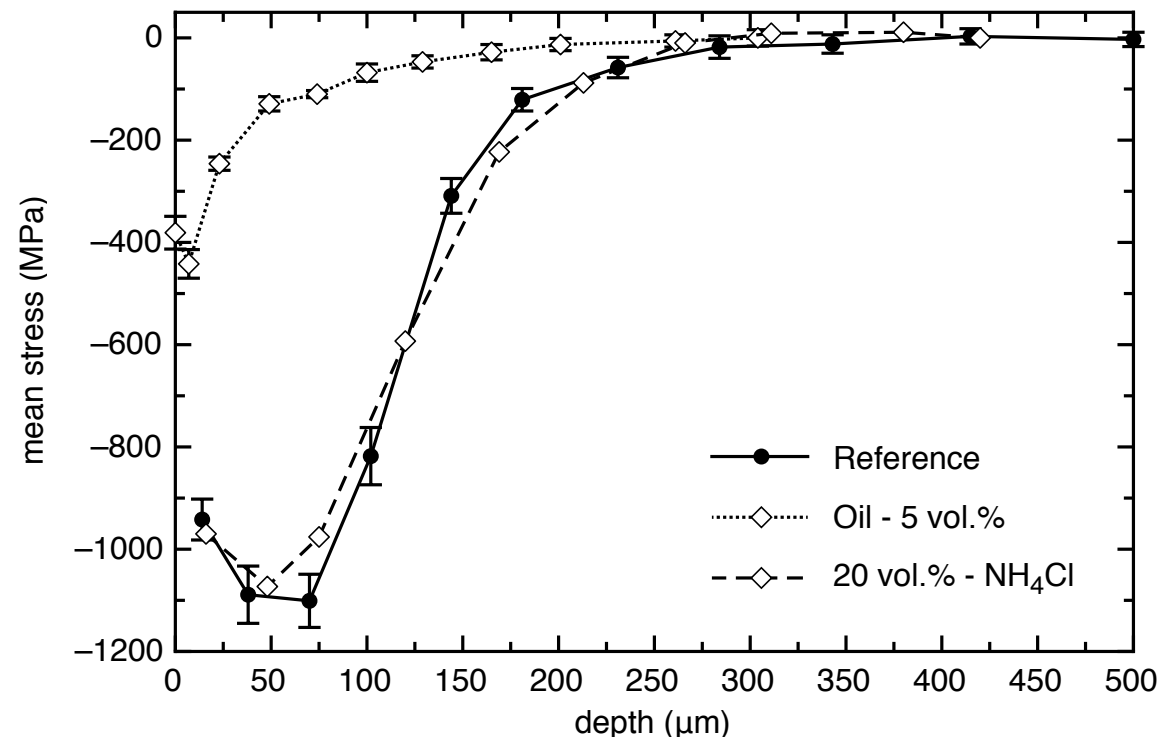
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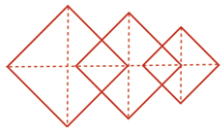




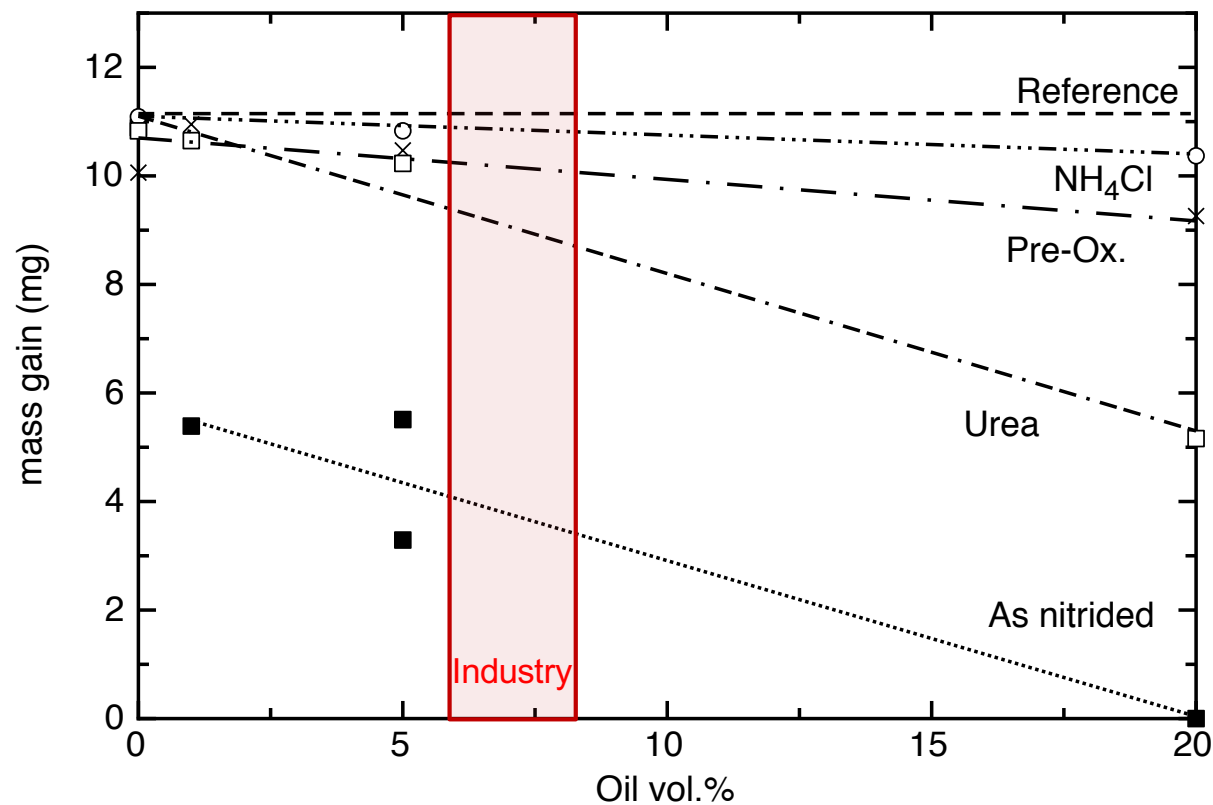
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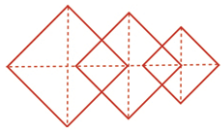
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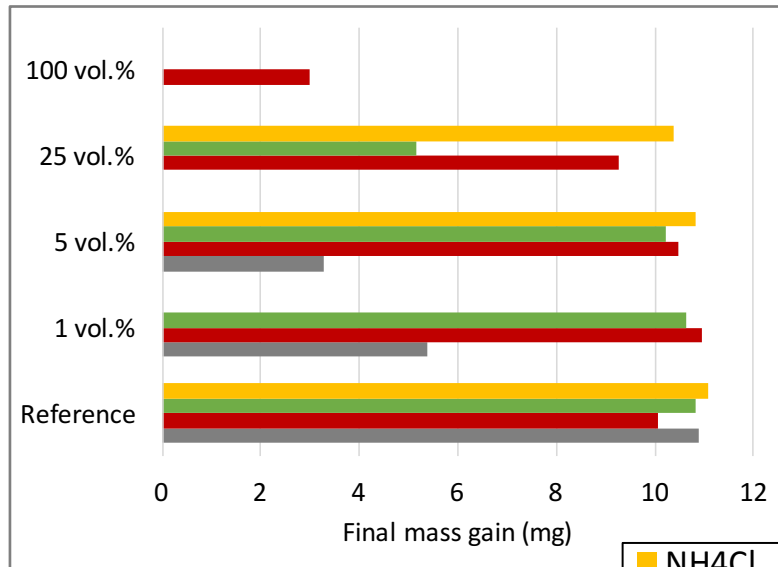


## 4. Conclusion (nitriding 520 °C, 5 h, $K_N$ 3,7 atm<sup>-1/2</sup>)

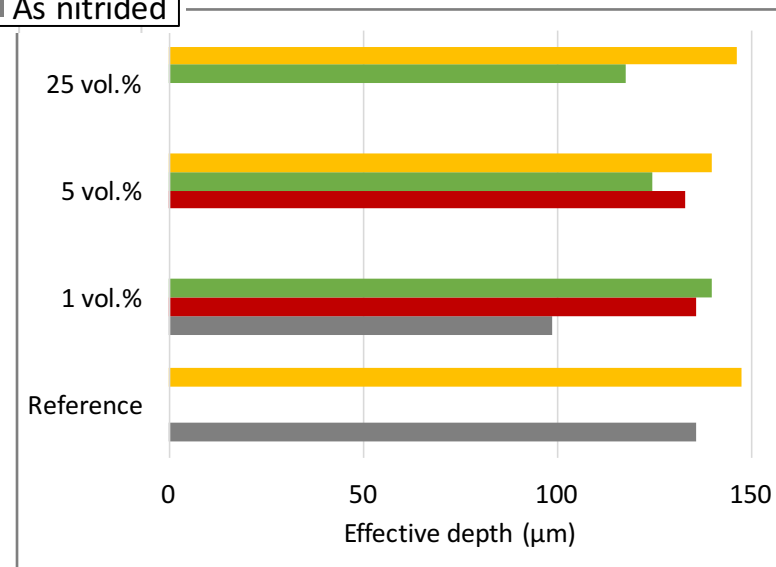
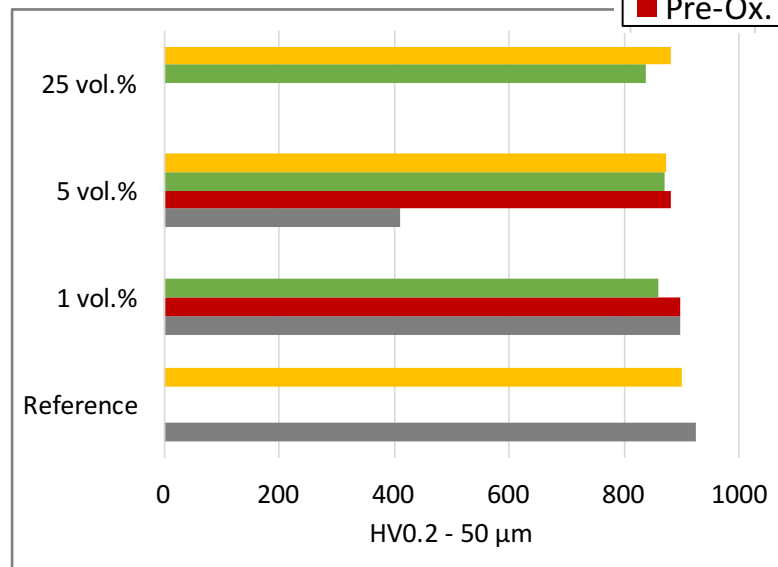




### 4. Conclusion (nitriding 520 °C, 5 h, $K_N$ 3,7 atm<sup>-1/2</sup>)



- In-situ pre-treatment:
  - Urea
  - Oxidization (thickness layer dependence)
  - NH<sub>4</sub>Cl
- Advantage:
  - In-situ (during the heating stage)
  - NH<sub>4</sub>Cl
    - Decomposition into NH<sub>3</sub>
    - Acidic cleaning/sanding



*Thank you for your  
attention !*

B.Guillot, S.Jégou, L.Barrallier, *Degradation of gaseous nitriding of steel by lubricant contamination - Effect of in-situ pre-treatments*, submitted to Surface & Coating Technology (2016)